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Research Article / Araştırma Makalesi

EFFECT OF GRAPHENE-TiO_2 ON THE PHOTODEGRADATION OF OLIVE MILL EFFLUENT AND RECOVERY OF GRAPHENE-TiO_2

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ABSTRACT

In this study, Graphene-TiO_2 was used to treat the pollutants from the olive mill industry wastewaters by photo-degradation. The large-scale production of functionalized graphene at low cost should result in good adsorbents for water purification due to the two-dimensional layer structure, large surface area, pore volume and presence of inorganic functional groups in the surface. The photo-removals of COD, total solid and total phenol in olive mill effluent wastewater with Graphene-TiO_2 were investigated under photocatalytic oxidation. The effects of increasing Graphene-TiO_2 concentrations (0.5 g/L, 1 g/L 3 g/L, 5 g/L and 10 g/L), photooxidation times (15, 30, 60 and 90 min) and pH (4, 7 and 10) were evaluated on the treatment of OMW pollutants. The photocatalytic reactions were performed under UV irradiation. The maximum pollutant removal efficiencies for COD, total phenol and TS obtained under 300 W UV light were 88%, 92% and 95% throughout photocatalysis at the optimum Graphene-TiO_2 concentration (3 g/L). The maximum recovery capacity of Graphene-TiO_2 was found between 90 and 95% after sequential six cycles.
Keywords: Graphene-TiO_2, photocatalytic degradation, olive mill wastewater, UV irradiation.

1. INTRODUCTION

Agro-industrial wastewaters such as olive-oil mill effluent wastewaters (OMW) are amongst the most polluting industrial effluents since they cause considerable environmental problems (coloring of receiving waters, a serious threat to aquatic life, pollution of surface and ground waters, alterations in soil quality, phytotoxicity and odor nuisance) [1]. OMW contains appreciable amount of organic materials with a high amount of toxicity/phytotoxicity-associated compounds, which resist biological degradation [2]. Treatment of OMWs is of great importance and very difficult due to the high organic, phenol, fatty acids, and suspended solids content [2]. Inadequate conventional treatment methods have led to alternative treatment methods such as treating OMW with nanoparticles. TiO_2-based materials are the most commonly used semiconductor oxide photocatalysts due to their low environmental impact. However, there are numerous obstacles impeding the maximization of photocatalytic activity in these materials, including low adsorption ability, detrimental recombination of charge carriers, and light utilization. TiO_2/carbon nanotube composites have been established as viable potential photo

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catalysts for use in both water and air purifications [3,4]. The synergetic effect of carbon nanotubes on photocatalyst enhancement, in which carbon nanotubes act as the electron sink for the hindrance of charge carrier recombination [1,2] or as the photosensitizer to generate a greater density of electron/hole pairs [5], has been previously demonstrated. Carbon nanotubes also behave as impurities, resulting in the formation of Ti–O–C bonds and, therefore, expanding the light absorption to longer wavelengths. Graphene, a new member of carbon materials, has been used as a support material for photocatalysts owing to its unique physical structure, large surface area, superior electrical conductivity and excellent adsorption capacity [6]. These properties make graphene a viable co-catalyst to accept electrons for exciton separation [5,6]. In TiO_2 photocatalysts combined with two-dimensional GO (GO– TiO_2) hybrids, the oxygenated functional groups on the GO sheets facilitate the binding of TiO_2 and GO [3,4] and GOs can serve as electron sinks under ultraviolet (UV) illumination or electron donors under visible light illumination for retardation of electron-hole recombination [5,6]. Additionally, the surface areas of GO– TiO_2 hybrids (e.g., 80 m^2g^{-1}) are higher than that of uncoupled TiO_2 (e.g., 57 m^2g^{-1}) [5]. The combination of TiO_2 and graphene oxide and/or graphene is predicted to generate a synergistic effect that potentially enhances the photodegradation of organic contaminants in aqueous media due to the possible improvements in the adsorb ability.

Therefore, in this work, it was aimed to determine photo-removals of COD, total solid (TS) and total phenol in OMW with Graphene-TiO_2 under photocatalytic oxidation. Photo-degradation under UV irradiation was studied for increasing irradiation times, pH and concentrations of Graphene-TiO_2.

2. MATERIAL AND METHODS

2.1. Wastewater and Chemicals

Olive mill effluent from an olive mill industry located in Aydın was collected and used without any pre-treatment in November 2013. Graphene and TiO_2 were bought externally. Demineralized water was used for preparation of reagents solutions. 0.1 M HCl and 0.1 M NaOH are used to adjust pH values of olive mill wastewater.

2.2. Photocatalytic Experiments

Treatment of OMW under UV experiments was conducted in an open batch system at room temperature of 20-25°C. Quartz glass reactors with volumes of 1100 ml and 20 UV lamps each one having an irradiation power of 15 Watt were used for the photocatalytic treatment with UV in a isolated stainless-steel device . The effects of concentrations of Graphene-TiO_2 (0.5 g/L, 1 g/L 3 g/L, 5 g/L and 10 g/L), irradiation times (15, 30, 60 and 90 min) and pH (4, 7, and 10) on the treatment of olive mill wastewater were investigated. The pollutants in the OMW were measured in the supernatants after the samples were centrifuged at 9000 rpm for 10 min. All the experiments data were found from the duplicates analysis and the results presented as the mean values of the duplicates samples.

2.3. Analytical procedures

COD was measured by colorimetric method (5220 D) as explained in detail in APHA (2005) with a Spectrophotometer Aquamate Thermo at 420 nm wave length. Phenol were measured using the Merck/WTW 14551 phenol reagent kits in a Photometer Nova 60/Spectroquant. TS measurements were performed according to method 2540B presented in Standard Methods (2005). Average concentrations and yields were found from the duplicate analysis of COD, total phenol and TS.

2.4. Preparatio n of Graphene-TiO_2 Under Laboratory Conditions

In a typical preparation, an aqueous dispersion of graphene (8.4 mg/mL) was dissolved in 200 mL of deionized water. TiO_2 powder (P25, Degussa) was dispersed in deionized water and subsequently added to the graphene oxide solution. The mixture was sonicated for 1.5 h and further stirred for 12 h at room temperature to obtain a homogeneous solution. The product was filtered and dried in a vacuum at 50°C for 4 h.

2.5. Reuse Method of Graphene-TiO_2

For reuse process after the Graphene-TiO_2 was used in the first photocatalytic degradation step was centrifuged and filtered from a membrane with a pore size of 0.45 µ and washed three times by water and ethanol and then was dried at an incubator at 45^{O}C during 1 hour. This Graphene-TiO_2 was used for the next sequential treatment. It was filtered and washed with ethanol and water and dried again. The same Graphene-TiO_2 was used five sequential times to treat the raw OMW in each step with UV irradiation. Under sunlight treatment the first used Graphene-TiO_2 was used threat the raw OMW.

3. RESULTS AND DISCUSSION

3.1. Wastewater Characterization

The average COD, TS, and phenol contents of the raw olive mill effluent were 117000 mg/L, 84250 mg/L, and 660 mg/L respectively, while its average pH value was between 4.0 and 4.1 (Table 1). The samples were stored at room temperature and shaken well before all the experiments.

Table 1. Characterization of olive mill wastewater

Parameters	Initial Value
COD	117000 ± 200mg/L
TS	84250± 300 mg/L
Phenol	660±12 mg/L
pH	4.0-4.1

3.2. The Effect of Concentration of Graphene-TiO_2 on Treatment of OMW under UV

Graphene-TiO_2 concentration is an important parameter for the photo-treatment of OMW. In order to determine the maximum photocatalytic treatment efficiencies of OMW 0.5 g/L, 1 g/L 3 g/L, 5 g/L and 10 g/L Graphene-TiO_2 concentrations were researched. Preliminary experiments showed that among the irradiation times that are tested, the maximum OMW removal was obtained after 30 min irradiation time (data not shown). Therefore, all experiments were realized after 30 min irradiation time, at 21°C (room temperature) and at original pH (4) of OMW and under 300 W UV power.

The COD removal yields were obtained as 44%, 62%, 88%, 88% and 79 % at 0.5 g/L, 1 g/L 3 g/L, 5 g/L and 10 g/L Graphene-TiO_2, respectively (Fig.1.a). The TS removal yields were obtained as 57%, 79%, 95%, 93% and 85% at 0.5 g/L, 1 g/L 3 g/L, 5 g/L and 10 g/L Graphene-TiO_2, respectively (Fig.1.b). The phenol removal yields were obtained as 55%, 72%, 92%, 90% and 82% at 0.5 g/L, 1 g/L 3 g/L, 5 g/L and 10 g/L Graphene-TiO_2, respectively (Fig.1.c). The results showed that the removal efficiencies were not changed with increasing Graphene-TiO_2 concentrations from 3 g/L up to 10 g/L, significantly (Fig.1). The photocatalytic reaction is mainly subject to the transmission of UV light. Due to scattering effect of the high level of suspended photocatalyst concentration, the transmission of UV light is greatly inhibited and this results in a sharp decrease in photocatalytic OH radical production [7].

Among the Graphene-TiO_2 concentrations (0.5, 1, 3, 5 and 10 g/L), it was found that the maximum COD, phenol and TS yields were found at 3 g/L Graphene-TiO_2 composite concentration. The maximum COD, TS, phenol removal yields were obtained 88%, 95% and 92%, respectively (Fig.1.d).

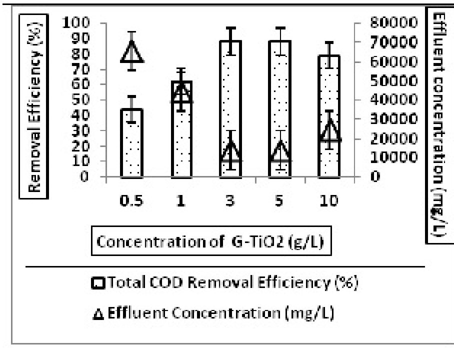

Fig.1.a. Effect of increasing Graphene-TiO_2 concentrations on COD removal from OMW (pH 4, T: 20°C, Irradiation time: 30 min)

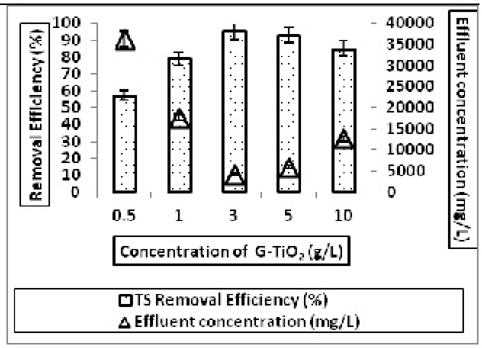

Fig.1.b. Effect of increasing Graphene-TiO_2 concentrations on TS removal from OMW (pH 4, T: 20°C, Irradiation time: 30 min)

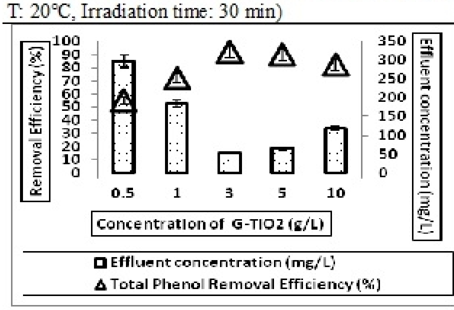

Fig.1.c. The effect of increasing Graphene-TiO_2 concentrations on Phenol removal from OMW (pH 4, T: 20 °C, Irradiation time: 30 min)

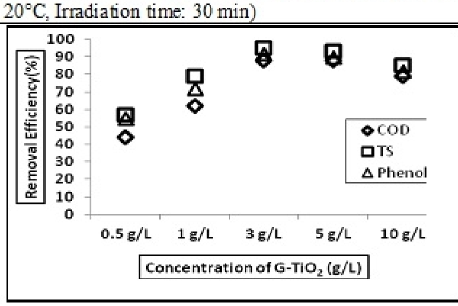

Fig.1.d. Illustration of removal yields of all pollutant parameters (pH 4, T: 20 °C, Irradiation time: 30 min)

Figure 1. The effect of concentration on COD, TS, phenol removal with UV irradiation

3.3. The Effect of Irradiation Time on Treatment of OMW under UV

OMW treatment with Graphene-TiO_2 was investigated at different irradiation times. Irradiation times were chosen as 15, 30, 60 and 90 min. The concentration of Graphene-TiO_2 was selected as 3 g/L to determine the optimum irradiation time. The irradiation time experiments realized in the original pH (4.0 - 4.1) of OMW at 20°C. The maximum removal efficiency of COD, TS and phenol were obtained at 30 min among the irradiation times used for experiments (Fig. 2). The COD removal yields were obtained as 67%, 88%, 90% and 77% at 15, 30, 60 and 90 min irradiation times, respectively. When the irradiation time was increased from 30 min to 60 min, the COD removal efficiency was not increased significantly (Fig. 2.a.). This situation can be explained as the formation of small colorless metabolite organic molecules at long retention times which, at least temporarily, remain in the solution, for instance ethanol, glycerol and simple sugars which can be considered as degradation intermediates as reported by El Hajjouji et al., 2008 [8]. The TS removal yields were obtained as 69%, 95%, 90% and 80% after 15, 30, 60 and 90 min irradiation times, respectively (Fig. 2.b.). Increasing the irradiation time from 30 min to 90 min decreased the removal efficiency of TS to 80%. These results imply that the presence of solid compounds in the OMW are resistant to further oxidation at long retention times since the maximum TS removal was observed after 30 min photooxidation. The decreased photodegradation efficiency at 90 min irradiation time may be explained as the reduction of the remaining active adsorption sites of Graphene-TiO_2.

The phenol removals were 63%, 92%, 88% and 72% at 15, 30, 60 and 90 min irradiation times, respectively (Fig. 2.c.). Decreasing the phenol removal efficiencies with the increasing of the irradiation time can be associated with metabolites of phenolic molecules such as para-coumaric acid and gallic acid can be formed during oxidation under the long irradiation time(data not shown).

Fig.2.d summarizes all the removal efficiencies of pollutants in the OMW after treatment with UV. The maximum COD, TS, phenol removal yields were obtained after 30 min irradiation time (Fig. 2.d.)

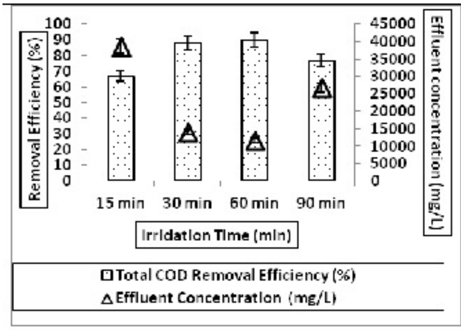

Fig. 2.a. The effect of irradiation time on COD removal efficiency (pH 4, Graphene-TiO_2 concentration: 3 g/L, T:20 °C)

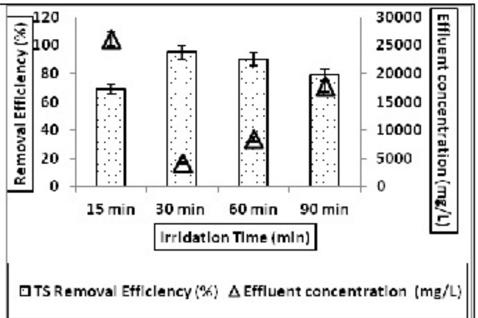

Fig. 2.b. The effect of irradiation time on TS removal efficiency (pH 4, Graphene-TiO_2 concentration: 3 g/L, T: 20 °C)

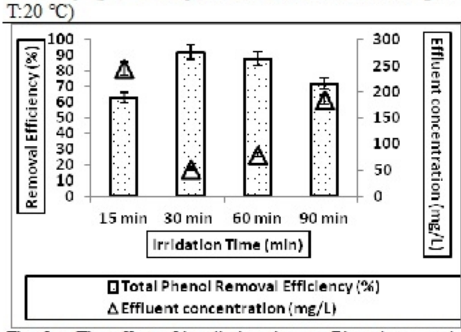

Fig. 2.c. The effect of irradiation time on Phenol removal efficiency (pH 4, Graphene-TiO_2 concentration: 3 g/L, T:20 °C)

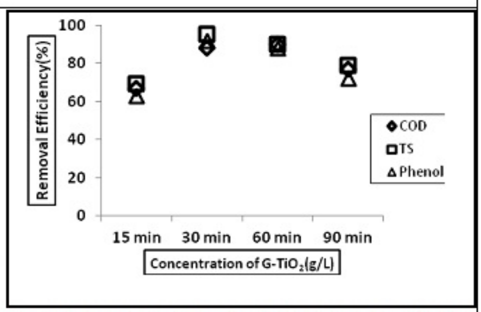

Fig. 2.d. Illustration of removal yields of all pollutant parameters (pH 4, Graphene-TiO_2 concentration: 3 g/L, T: 20 °C)

Figure 2. The effect of irradiation times on COD, TS, phenol removal with UV irradiation

3.4. The Effect of pH of OMW on Treatment of Olive Mill Treatment with Graphene-TiO_2

pH of OMW is an important parameter for the treatment mechanism of olive mill wastewater. In this study, the effect of acidic, neutral and alkaline pH was investigated on the treatment efficiency on OMW with Graphene-TiO_2. (Fig. 3). All experiments were realized with 3 g/L Graphene-TiO_2 at 30 min retention times at 20 °C. The pH values of OMW were adjusted to 7 and 10 from the original pH of 4- 4.1 by adding 0.1 M HCl and 0.1 NaOH solutions, The addition of alkaline and acid chemicals to adjust the pH of OMW increase the cost of the treatment. Increasing of pH from 4 up to 10 did not significantly affect the COD, TS and phenol removal efficiencies. The maximum COD, TS, phenol removal yields were obtained as 88%, 95% and 92% at pH 4, respectively which is the original pH of OMW . Therefore pH 4 was selected as the optimum pH for the photodegradation of all pollutant parameters among used pH values. The isoelectric point (pI)/point of zero charge (pzc) of graphene plays a key role in a number of physico-chemical phenomena occurring at the graphene-liquid interface. The pI of bare graphene (as-prepared, chemical vapor deposition (CVD)-grown) is found to be less than 3.3 [9].

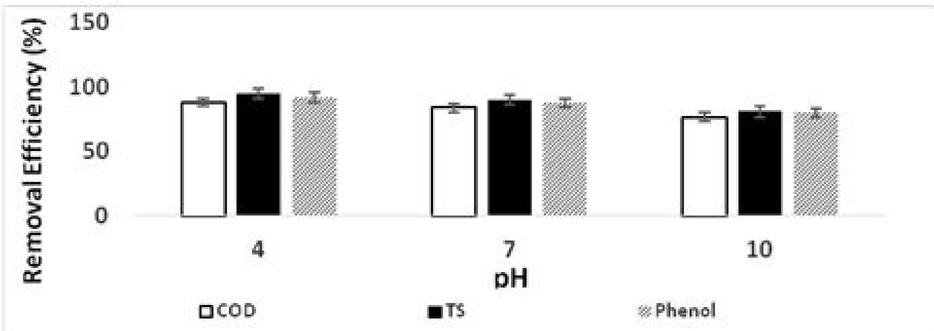

Figure 3. Effect of pH on the treatment of OMW with Graphene-TiO_2 composite on COD, TS, and Phenol yields in the OMW

3.5. Reuse of Graphene-TiO_2 after treatment of OMW

In this study, six sequential treatment steps were investigated for determination of reusability of Graphene-TiO_2. After the Graphene-TiO_2 was first used in the treatment of OMW pollutants under UV centrifuged, filtered and washed with distilled water and ethanol to use again under six sequential treatments of OMW under the same operational conditions (pH 4, Graphene-TiO_2 concentration: 3 g/L, T: 20°C) were performed. After each sequential treatment the same polluted 3 g/L Graphene-TiO_2 was cleaned as reported above . After 2^{ND} and 3^{TH} sequentials it was found that with 3 g/L Graphene-TiO_2 the COD, phenol and TS yields were not changed compared to the first use of Graphene-TiO_2 (Fig. 4a). It was found that the removals of all parameters decreased slightly after 5^{TH} and 6^{TH} steps of treatment. As a consequence, the yields of Graphene-TiO_2 recoveries for each treatment steps (1, 2, 3, 4, 5 and 6^{TH}) were obtained as 95%, 95%, 94%, 93%, 93% and 90%, respectively (Fig.4b). In the study performed by Zhang et al., (2017) [10] Graphene-TiO_2 composite was recovered by a yield of 89% after 2^{TH} utilization.

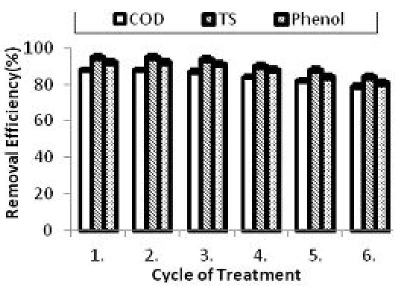

Fig.4a. Reuse cycles of treatment of OMW with UV (pH 4, concentration of Graphene-TiO$_2$: 3 g/L, T: 20 °C, irradiation time: 30 min)

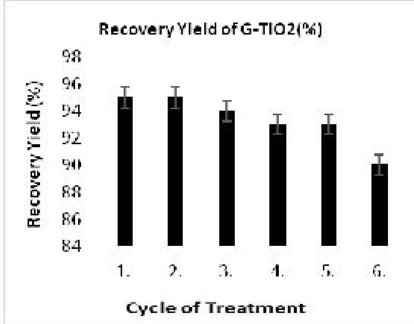

Fig.4b. Recovery yield of Graphene-TiO$_2$ under same operational conditions (pH 4, concentration of Graphene-TiO$_2$: 3 g/L, T: 20 °C, irradiation time: 30 min)

3.6. Optimum operational conditions and cost analysis

For maximum removals of OMW pollutants (> 94%) the optimized operational conditions were 300 W UV power, 3 g/L Graphene-TiO$_2$ concentration, 30 min irradiation time at original pH of OMW(4.0-4.1) at a photoreactor volume of 1100 ml with a Graphene-TiO$_2$ recovery yield of 93%. The cost spent to the photoreactor, to UV lamps, to Graphene-TiO$_2$ concentration, to device containing the photoreactors and the UV lamps were 0.2 Euro, 0.2 Euro, 0.3 Euro and 0.6 Euro to treat 1100 ml OMW wastewater. The labour cost and laboratory cost takes 0.1 Euro. The total cost to treat 1100 ml OMW wastewater was found to be 1.4 euro. The cost of the adjustment of OMW pH with alkaline and acidic solutions was 1.9 Euro. The total cost was calculated as 140 Euro to treat 100 L OMW under real scale land applications.

4. CONCLUSION

In this study, Graphene-TiO$_2$ was produced under laboratory conditions and it was used effectively to treat the pollutants in the OMW. The maximum COD, TS and phenol yields were 88%, 95% and 92% with 3 g/L Graphene-TiO$_2$ after 30 min UV irradiation at original pH of OMW (4.0-4.1) under 300 W UV. The old polluted Graphene-TiO$_2$ can be effectively used again after 5 sequential with a recovery yield of 93% to treat the new raw OMW from the pollutants. The total cost to treat the 1100 ml OMW wastewater under optimized condition was 1.4 Euro.

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